

# PATENT SPECIFICATION

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- (72) Inventor IRWIN LEONARD BREIER and ADRIANE MARSHA MOSS



## (54) A PROCESS FOR PREPARING 2,2-DI(4-HYDROXYPHENYL) PROPANE OF A HIGH DEGREE OF PURITY

(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The invention relates to a process for purifying 2,2-di(4-hydroxyphenyl)propane.

2,2-di(4-hydroxyphenyl)propane, as obtained by conventional preparation methods, contains small amounts, e.g., up to about five 15 percent by weight of by-products which cannot easily be removed. However, 2,2-di(4-hydroxyphenyl)propane of such a degree of purity is suitable for many applications in the synthesis and preparation of diverse products including,

20 for example, so-called epoxy resins and surface coatings on the basis of such resins. For some recently developed applications 2,2-di(4-hydroxyphenyl)propane of very high purity, i.e., having less than one-half percent by 25 weight impurities, is required, e.g., for the production of certain high molecular weight linear polymers. The presence of impurities in amounts of more than about three tenths of one percent by weight cannot even be tolerated.

30 In the production of polyarylcarbonate resins. In addition, for the production of premium grade resins, colour-free, i.e., extremely white 2,2-di(4-hydroxyphenyl)propane is required.

Purification methods so far tried out have 35 been found to be inadequate or at all events too expensive for commercial-scale operation. Distillation procedures generally fail to remove relatively involatile impurities. Crystallization from conventional organic solvents, e.g. chlorobenzene, may be satisfactory as regards 40 removal of impurities but then they give poor yields of the purified product. Procedures involving washing with recrystallizing from, or otherwise treating with large quantities of

water are economically burdened by the necessity of recovering phenolic components from dilute solution or treating the water prior to disposal, to avoid contamination of receiving water.

Surprisingly, the process of the present invention has been found suitable and economically attractive for purifying 2,2-di(4-hydroxyphenyl)propane.

According to the invention a process for purifying 2,2-di(4-hydroxyphenyl) propane comprises cooling a single-phase liquid mixture of 2,2-di(4-hydroxyphenyl) propane, phenol, and from 3 to 48%wt on phenol of water to a temperature at which an equimolar adduct of 2,2-di(4-hydroxyphenyl) propane and phenol crystallizes, separating the crystals so formed and removing the phenol component therefrom to yield purified 2,2-di(4-hydroxyphenyl) propane. Preferably the weight ratio of phenol to 2,2-di(4-hydroxyphenyl) propane in the starting mixture is in the range of from 0.9:1 to 10:1, more preferably in the range of from 1.2:1 to 8:1, and most preferably in the range of from 1.4:1 to 5:1.

Preferably, the single-phase liquid mixture contains from 10 to 46%wt on phenol of water.

The single-phase liquid mixture is cooled, preferably from a temperature of above 32°C, more preferably from a temperature in the range of from 32° to 77°C (90° to 170°F), most preferably in the range of from 38° to 77°C (100° to 170°F).

The single-phase liquid mixture may be cooled by conventional means, preferably to a temperature in the range of from 10° to 55°C (50°F to 130°F), and preferably with agitation, whereupon large crystals of exceptional purity form. When the process according to the invention comprises batch crystallization, cooling rates from approximately 1° to 10°C (approximately 2° to 15°F) per hour are suitable, but higher or lower cooling rates

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may also be effective. When the process of the invention comprises continuous crystallization, residence times of the crystals in the crystallization medium of from 0.5 to 10 hours or more are suitable, residence times of from 1 to 3 hours being preferred. The crystals may be separated from the liquid by conventional separating means, including e.g., decantation, filtration and centrifugation. Unexpectedly, it has been found that the crystals formed in this medium have high impact resistance, leading to growth of comparatively large crystals and thereby facilitating ease of separation from the liquid medium with little, if any, fragmentation.

Advantageously, the mother liquor is freed of water by known drying means such as extraction with solvents in which water has preferential solubility, and the dried liquid recycled, in whole or in part, to be used in the purification of additional amounts of 2,2-di(4-hydroxyphenyl)propane. Preferably, the water is recovered from the mother liquor by simple distillation, and is, at least in part, added as make-up material to a fresh amount of single-phase liquid mixture.

The separated crystals may optionally be rinsed with a non-solvent for the 2,2-di(4-hydroxyphenyl)propane including solvents such as hydroxyaryls, e.g. phenol, chloro-alkanes, e.g. ethylene dichloride, and chloro-alkyls. It is, however, found that, generally, such rinsing is not essential to the attainment of the desired high degree of purity. If, however, rinsing is to be carried out, phenol, in particular aqueous phenol, may suitably be employed. At all events the phenol is finally removed from the crystals. To this end any known method may be employed, e.g., extraction with a solvent in which phenol is preferentially dissolved, or distillation. In the latter case the crystals are to be heated, if necessary or desired under reduced pressure. Preferably, the heating temperature should not be allowed to exceed 305°C (400°F) when stripping the crystals of phenol, to prevent thermal dissociation and degradation of the product.

The process of the invention may be carried out batchwise, continuously or semi-continuously. The single-phase liquid mixture may be formed by combining the ingredients in any order; however, it is convenient to add the impure 2,2-di(4-hydroxyphenyl)propane to the phenol premixed with water and at an elevated temperature, preferably, the temperature which the single-phase liquid mixture must have prior to cooling, as discussed in the above. Instead of impure 2,2-di(4-hydroxyphenyl)propane also the equimolar adduct of 2,2-di(4-hydroxyphenyl)propane and phenol can be added to phenol premixed with water, if the said adduct is of a lesser degree of purity, so that upon removal of phenol it would yield 2,2 - di(4 - hydroxyphenyl)propane of insufficient purity. In particular such an impure

adduct may be obtained from a reaction mixture resulting from the condensation of phenol and acetone, which contains unconverted phenol, the said reaction mixture being subjected to a distillation for removing water, unreacted acetone, and gaseous impurities, after which the remaining mixture is cooled to a temperature at which the said adduct crystallizes, the crystals finally being separated from the liquid.

A condensation reaction of phenol and acetone, as just referred to, may, e.g. be carried out in continuous operation, generally with a molar excess of phenol to acetone, e.g., in the range of from 3:1 to 25:1, and in the presence of a volatile acidic catalyst, including, e.g., hydrogen chloride, hydrogen bromide, and boron trifluoride, at a temperature in the range of from approximately 20° to 85°C (approximately 70 to 185°F). The reaction may be promoted by the addition of a sulphur-containing compound known to be active as a promoter, e.g., methyl mercaptan, sulphonyl chloride, hydrogen sulphide and butyl mercaptan. The reaction mixture may be continuously withdrawn and dried by a distillation step to remove the water formed in the reaction, together with any unconverted acetone and volatile impurities including catalyst and/or promoter when they are volatile. These may advantageously be dried by conventional means and recycled to the reaction zone. The ratio of unreacted phenol to the desired product in the dried reaction mixture may vary considerably in accordance with the specific operating conditions, but is suitably adjusted in the range of from 0.9:1 to 10:1, preferably from 1.2:1 to 8:1. Such ratios may be achieved as a natural consequence of charging an excess of phenol to acetone in the reaction, by partial removal of excess of unreacted phenol by e.g., fractionation, or by supplemental addition of phenol. The reaction mixture after being heated to elevated temperatures during the drying step, is then brought to a temperature in the range between approximately 45° and 70°C (approximately 110 and 160°F) by cooling means to form a solid crystalline material and a mother liquid comprising phenol and impurities. Preferably this first crystallization step is carried out in an essentially anhydrous medium, i.e., containing less than about 0.1% by weight of water. The crystalline material may be separated by conventional separating means including, e.g., decantation, filtration, and centrifugation. The mother liquid may advantageously be recycled entirely or in part to the reaction zone for conversion to additional product. When the process according to the invention comprises batch crystallization, the separated crystals are combined with phenol and water, which may be added either as individual streams or together in the form of an aqueous phenol, to form the single-phase liquid mixture from which puri-

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fied adduct crystals are to be obtained.

It is a particular advantage of the process of the invention that all types of impurities are removed. The impurities include varying amounts of the 2,4'-dihydroxy isomer, trisphenols and certain intramolecular condensation products having mono-functionality, e.g., p - (2,2,4 - trimethyl - 4 - chromanyl)phenol and its isomers as well as colour forming impurities of undetermined structure. As is known to those skilled in polymerization chemistry, the 2,4' - dihydroxy isomers disrupt polymer symmetry and inhibit high molecular weight as do the intra-molecular condensation products. On the other hand, trisphenols resulting, e.g., from the condensation of two moles of acetone and three moles of phenol can alter ultimate polymer properties by causing branching or even gelation through cross-linking.

Because, as will be seen in the following Examples, all impurities, i.e. both high melting impurities, e.g. triphenol (m.p. about 195°C), and low melting impurities, e.g. 2-(2-hydroxyphenyl) 2 - (4 - hydroxyphenyl)propane (m.p. 110°C), as well as colour impurities are reduced to extremely low levels by the process of the invention, the traditional criterion of freezing point as a measure of product purity becomes unsatisfactory. However, as is known to those skilled in the art, a most rigorous test for colour impurities in 2,2 - di(4 - hydroxyphenyl)propane is the so-called APHA colour (platinum cobalt colour standards) in alkaline aqueous solution. It is an especial advantage that the process according to the invention can produce a product having a caustic colour less than 60 APHA.

**EXAMPLE I.**

23 Parts by weight of a commercial technical grade 2,2-di(4-hydroxyphenyl)propane of 96 % wt purity, having a caustic APHA colour of 112 and freezing point of 154.6, were added to 77 parts by weight of phenol

containing 10 % wt on phenol of distilled water, and heated to a temperature of approximately 57°C (approximately 135°F). A single-phase mixture formed, which was allowed to cool with gentle stirring for eight hours to a temperature of 32°C (90°F). Large crystals formed of an adduct in equimolar proportions of 2,2-di(4-hydroxyphenyl)propane and phenol. These crystals were readily separated from the liquid without damage by filtration in a Buchner funnel and then rinsed with phenol in an amount of 0.6 parts by weight per part by weight of filter cake to remove entrained liquid. The adduct crystals were then heated under a vacuum of approximately 20 mm of mercury to a final temperature of approximately 199°C (approximately 390°F) to strip the phenol component, purified 2,2-di(4-hydroxyphenyl)propane remaining behind.

The procedure was repeated with another commercial technical grade 2,2-di(4-hydroxyphenyl)propane of the same degree of purity, having a caustic APHA colour of 207 and a freezing point of 154.1. 35 Parts by weight of this 2,2-di(4-hydroxyphenyl)propane were added to 65 parts by weight of phenol containing approximately 33 % wt on phenol of distilled water.

The procedure was repeated with the same technical grade 2,2 - di(4 - hydroxyphenyl)-propane as in the first experiment described. 37 Parts by weight of this 2,2-di(4-hydroxyphenyl)propane were added to 63 parts by weight of phenol containing 40 %wt on phenol of distilled water.

The results obtained in these experiments are shown in the following Table, which also contains data regarding 2,2 - di(4 - hydroxyphenyl)propane obtained from adduct crystals which had not been subjected to a phenol rinse, prior to the heating for stripping off phenol. Such products are already quite satisfactory for a number of practical purposes.

TABLE I

Properties	Experiment No. 1		Experiment No. 2		Experiment No. 3	
	Prior to phenol rinse	After phenol rinse	Prior to phenol rinse	After phenol rinse	Prior to phenol rinse	After phenol rinse
APHA colour, measured on solution of 50 grams in 70m l of methanol	—	18	—	45	—	13
Caustic APHA colour	—	75	—	106	92	37
GLC Analysis (% wt.)						
2-(2-hydroxyphenyl)-2-(4-hydroxyphenyl)propane	0.35	0.06	1.43	0.32	—	0.09
Isomers of p-(2,2,4-trimethyl-4-chromanyl)-phenol	0.05	0.03	0.05	0.03	—	0.01
Trisphenol	0.07	0.01	0.30	0.04	—	0.07
2,2-di-(4-hydroxyphenyl)-propane (by difference)	99.5	99.9	98.2	99.6	—	99.83

5 Separation in the gas-liquid chromatography (GLC) analysis was achieved by injection of the trimethyl silyl ether derivatives of the sample in a column packed with a dimethyl silicone gum sold under the trade name "OV-1" on glass beads and quantified by a hydrogen flame detector.

10 The caustic APHA colour was measured on a solution of 7.5 grams of 2,2-di(4-hydroxyphenyl)propane in 50 ml of 1.5 N aqueous sodium hydroxide after 10 minutes at 25 to 30°C.

#### EXAMPLE II.

15 2,2 - Di(4 - hydroxyphenyl)propane was produced in a continuous operation in an autoclave by reacting phenol with acetone in a mole ratio of 6:1 in the presence of hydrogen chloride and methyl mercaptan at a temperature of approximately 55°C (approximately 130°F). Water formed during the reaction, unreacted acetone, and gaseous impurities such as catalyst and promoter, were distilled off from the resulting reaction mixture which was then cooled to approximately 57°C (approximately 135°F). Crystals formed of an adduct comprising equimolar amounts of 2,2-di(4-hydroxyphenyl)propane and unreacted phenol. This adduct was not yet of the desired high degree of purity, and was, therefore, subjected

to the purification treatment of the invention. It was, accordingly, combined with heated phenol and water in amounts sufficient to produce a single-phase liquid mixture at approximately 60°C (approximately 140°F) comprising approximately 34% wt of 2,2-di(4-hydroxyphenyl)propane, phenol in a weight ratio of 2,2-di(4-hydroxyphenyl)propane of 1.5:1, and 35% wt on phenol of water. This mixture was cooled, with gentle stirring, to approximately 24°C (approximately 75°F) in approximately four hours. Relatively large adduct crystals formed, which were separated by centrifuging at 24°C (75°F). The crystals were rinsed with aqueous phenol, containing approximately 10% wt on phenol of water, in an amount of approximately 0.35 parts by weight per part by weight of crystals. Then the crystals were stripped of phenol by heating under vacuum of approximately 1 millimeter of mercury, absolute, to a terminal temperature of approximately 202°C (approximately 395°F). The molten 2,2-di(4-hydroxyphenyl)propane, obtained as the residue, was cooled to solidify and had the properties shown in the following Table, which, for comparison, also shows the properties of 2,2-di(4-hydroxyphenyl)methane obtained from the adduct as first isolated and not yet subjected to the treatment of the invention.

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TABLE II

Properties	From first adduct	From final adduct
APHA colour, measured on solution of 50 grams in 70 ml of methanol	27	12
Caustic APHA colour	112	39
Freezing point (°C)	154.5	157.0
GLC Analysis (% wt)		
2-(2-hydroxyphenyl)-2-(4-hydroxyphenyl)propane	0.3	0.04
Isomers of p-(2,2,4-trimethyl-4-chromanyl)phenol	2.7	0.03
Trisphenol	1.0	0.008
2,2-di-(4-hydroxyphenyl)propane (by difference)	96.0	99.92

The GLC-analysis and the determination of the caustic ALPHA colour were carried out as in Example I. The freezing point was determined according to ASTM method D-1015-55.

WHAT WE CLAIM IS:—

1. A process for purifying 2,2-di-(4-hydroxy) propane, which comprises cooling a single-phase liquid mixture of 2,2-di-(4-hydroxyphenyl) propane, phenol, and from 3 to 48 %, wt on phenol of water to a temperature at which an equimolar adduct of 2,2-di-(4-hydroxyphenyl) propane and phenol crystallizes, separating the crystals so formed and removing the phenol component therefrom to yield purified 2,2-di-(4-hydroxyphenyl) propane.
2. A process as claimed in claim 1 wherein the crystals are washed with a non-solvent for 2,2 - di - (4 - hydroxyphenyl) propane prior to the removal from the crystals of the phenol component.
3. A process as claimed in claim 1 or claim 2, wherein in the single-phase liquid mixture the weight ratio of phenol to 2,2-di-(4-hydroxyphenyl) propane is in the range of from 0.9:1 to 10:1.
4. A process as claimed in claim 3, wherein in the single-phase liquid mixture the weight ratio of phenol to 2,2-di-(4-hydroxyphenyl) propane is in the range of from 1.2:1 to 8:1.
5. A process as claimed in claim 4, wherein in the single-phase liquid mixture the weight ratio of phenol to 2,2-di-(4-hydroxyphenyl) propane is in the range of from 1.4:1 to 5:1.
6. A process as claimed in any one of the preceding claims, wherein the single-phase liquid mixture contains from 10 to 46 % wt on phenol of water.
7. A process as claimed in any one of the preceding claims, wherein the single-phase liquid mixture is cooled from a temperature of above 32°C (90°F).
8. A process as claimed in claim 7, wherein the single-phase liquid mixture is cooled from a temperature in the range of from 32° to 77°C (90° to 170°F).
9. A process as claimed in claim 8, wherein the single-phase liquid mixture is cooled from a temperature in the range of from 38° to 77°C (100° to 170°F).
10. A process as claimed in any one of the preceding claims, wherein the single-phase liquid mixture is cooled to a temperature in the range of from 10° to 55°C (50° to 130°F) to effect crystallization of the adduct.
11. A process as claimed in any one of the preceding claims, wherein the cooling is carried out with agitation.
12. A process as claimed in any one of the preceding claims, wherein prior to the removal of the phenol component, the crystals are rinsed with phenol.
13. A process as claimed in claim 12, wherein prior to the removal of the phenol component, the crystals are washed with aqueous phenol.
14. A process as claimed in any one of the preceding claims wherein the removal of the phenol component from the crystals is effected by heating, if necessary or desired under reduced pressure.

15. A process as claimed in claim 14, wherein the removal of the phenol component from the crystals is effected by heating under reduced pressure. 35

5 16. A process as claimed in any one of the preceding claims, wherein the single-phase liquid mixture has been obtained by combining an amount of an equimolar adduct of 2,2-di-(4-hydroxyphenyl) propane and phenol of lesser purity, with phenol premixed with water, which upon removal of phenol would yield 2,2 - di - (4 - hydroxyphenyl) propane of insufficient purity, with phenol and water. 40

10 17. A process as claimed in claim 16, 45

15 wherein the impure equimolar adduct of 2,2-di - (4 - hydroxyphenyl) propane and phenol has been obtained from a reaction mixture resulting from the condensation of phenol and acetone, which contains unconverted phenol, 50

20 the said reaction mixture being subjected to a distillation for removing water, unreacted acetone, and gaseous impurities, after which the remaining mixture is cooled to a temperature at which the said adduct crystallizes, the 55

25 crystals finally being separated from the liquid.

18. A process as claimed in claim 17, wherein phenol and acetone is charged to the reaction zone for effecting their condensation in a ratio of at least 3 moles of phenol per 30 mole of acetone.

19. A process as claimed in claim 17 or 18,

wherein the condensation of phenol and acetone is effected in the presence of a volatile acidic catalyst. 35

20. A process as claimed in claim 19, wherein the acid catalyst is hydrogen chloride. 35

21. A process as claimed in claim 20, wherein the reaction zone also contains a sulphur-containing promoter. 40

22. A process as claimed in any one of the preceding claims, wherein water is separated from the mother liquid remaining after separation of the crystalline equimolar adduct of 2,2-di-(4-hydroxyphenyl) propane and phenol formed upon cooling of the single-phase liquid mixture, the substantially anhydrous liquid obtained by the removal of water from the said mother liquid being, at least in part, added as make-up material to a fresh amount of single-phase liquid mixture. 45

23. A process for purifying 2,2-di-(4-hydroxyphenyl) propane as claimed in claim 1 and substantially as hereinbefore described with particular reference to the Examples. 50

24. 2,2 - Di - (4 - hydroxyphenyl) propane whenever purified by means of a process as claimed in any one of the preceding claims. 55

R. C. ROGERS,  
Chartered Patent Agent,  
Shell Centre, London, S.E.1,  
Agent for the Applicants.

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